Low eutectic temperature alloy diffusion process for hot-deformed Nd-Fe-B magnet

T. Akiya[1], H. Sepheri-Amin[1], J. Liu[1,2], L. Liu[1,2], T. Ohkubo[1], K. Hioki[3], A. Hattori[3], K. Hono[1,2]
[1]Elements Strategy Initiative Center for Magnetic Materials, National Institute for Materials Science
[2]Graduate School of Pure and Applied Science, University of Tsukuba
[3]Daido Steel Co. Ltd.

Nd-Fe-B magnets have been studied for more than thirty years. One of main research issues of Nd-Fe-B magnet is low thermal stability due to its low Curie temperature (T_c ~ 310°C). To improve the thermal stability, coercivity (H_c) enhancement is a possible way. For example, H_c of 3 T at room temperature (RT) is required for hybrid or pure electric vehicle and wind turbine generator to prevent a thermal demagnetization.

Coercivity of permanent magnet relates to the magnetocrystalline anisotropy field, H_a. The H_a of $Nd_2Fe_{14}B$ phase is about 7 T at RT and the value is theoretical maximum limit of coercivity. However, the coercivity of Nd-Fe-B magnet produced by conventional mass production route is only 1 T without Dy. It is accepted that the surface defects on $Nd_2Fe_{14}B$ particle and inclusions causes the degradation of coercivity, because the nucleation of reversed magnetic domain may occur at these sites. Here, $(Nd,Dy)_2Fe_{14}B$ phase possesses a higher magnetocrystalline anisotropy field than $Nd_2Fe_{14}B$. Therefore, Dy-rich shell structure formed by grain boundary (GB) diffusion process enhances the coercivity effectively with minimum amount of Dy for sintered magnet[1)].

It is empirically known that the coercivity of Nd-Fe-B magnet can be increased by refinement of $Nd_2Fe_{14}B$ crystals without Dy. A Nd-Fe-B sintered magnet with H_c ~ 2 T without Dy had been reported by Intermetallics Co.[2)]. They prepared fine $Nd_2Fe_{14}B$ powder with about 1 μm diameter by He-gas jet-milling technique. However, it is difficult to obtain sub-micron sized powder by jet-milling or any mechanical pulverization technique while preventing oxidation of the powders. Ultrafine $Nd_2Fe_{14}B$ crystal can be obtained by Hydrogenation-Decrepitation-Desorption-Recombination (HDDR) technique or die up setting process of rapidly quenched Nd-Fe-B alloy and then hot-deform processed magnet. These crystal sizes are one order of magnitude smaller than that of sintered magnet, about 300 nm in diameter particle (HDDR) and 300 nm in width and 50 nm in height of platelet shaped grain (hot-deformed), respectively. However, the reported coercivity of ultra-fine grain sized Nd-Fe-B HDDR powders and hot-deformed magnets is only around 1.5 T. This value is lower than expected from a trend of sintered Nd-Fe-B magnet, H_c ~ 2.5 T at 300 nm in diameter[3)].

We have studied the reasons of the low coercivity in three kind of Nd-Fe-B magnets, sintered[4, 5)], HDDR processed powder[6)] and hot deformed Nd-Fe-B magnet[7)]. In any case, the coercivity of Nd-Fe-B magnet relates to structure and chemistry of GB. It have been found that the GB of high coercivity magnet is thicker and contains lower Fe concentration[7)]. Fe-rich GB phase shows ferromagnetic property[5)], therefore, such ferromagnetic GB causes the magnetic coupling between $Nd_2Fe_{14}B$ grains. Thus, magnetic isolation between $Nd_2Fe_{14}B$ grains by nonmagnetic GB layer is critical point to enhance the coercivity.

We demonstrated that the low eutectic alloy diffusion technique is suitable way to modify the structure/chemistry of the grain boundary phase and enhance the coercivity in HDDR powder and hot-deformed magnet. This technique was independently reported by Sepehri-Amin *et al.*[6)] and Mishima *et al.*[8)] in the HDDR processed magnet powders. A low eutectic temperature alloy, such as Nd-Cu, Nd-Al and so on, infiltrates into GB rapidly in HDDR processed powder and hot-deformed magnet and thicker GB layer is formed between $Nd_2Fe_{14}B$ grains without significant grain growth. While, in sintered magnet, Cu diffuses into GB rapidly but the microstructure remains almost unchanged. Thus, the effect of Nd-Cu diffusion process is small in sintered Nd-Fe-B magnet.

Currently, we are focusing on the low eutectic temperature alloy diffusion process for hot deformed magnet. We have observed a coercivity enhancement from 1.5 T to 2.3 T using Nd-Cu eutectic alloy[9)], and 1.6 T to 2.6 T using

$Nd_{60}Dy_{20}Cu_{20}$ near-eutectic alloy[10] for small hot-deformed magnet with 1 mm thickness. While, remanence reduction of about 20 % was also observed due to infiltration of much amount of nonmagnetic material into magnet. After these works, we applied the technique to larger hot-deformed magnet with 5.6 mm thickness, and we confirmed that the infiltration effect occurs almost homogeneously and the coercivity enhancement occurs same as small specimen[11]. In addition, we observed sample expansion to mainly easy direction. The amount of diffusion alloy and volume expansion of magnet was almost comparable. So, we tried an expansion constraint method during diffusion process to prevent the excess diffusion of Nd-Cu phase[12]. As a result, we observed that the diffusion processed hot deformed magnet with constraint possesses higher remanence (M_r = 1.36 T) than simply diffusion processed one (M_r = 1.27 T). One of the reasons can be estimated that the diffusion processed magnet under constraint maintains the higher crystallographic texture than that of as hot-deformed and diffusion processed magnet without applying expansion constraint.

Temperature dependence of H_c and energy density [$(BH)_{max}$] of hot-deformed magnet and the samples that were Nd-Cu diffusion processed with and without an expansion constraint are shown in figure. For comparison, the energy densities of commercial 4% Dy and 8% Dy sintered magnets are also shown[13]. The temperature dependence of coercivity of Nd-Cu diffusion processed magnet is much better than original hot-deformed magnet and 4% Dy sintered magnet. This data suggests that the effect of ultrafine grain $Nd_2Fe_{14}B$ crystals appears by magnetic isolation in high temperature. In addition, the $(BH)_{max}$ of expansion constraint processed hot-deformed magnet is 358 kJ/m^3 at RT and 191 kJ/m^3 at 200 ˚C. This high-temperature property is slightly higher than that of Dy 4% sintered magnet.

We modified the GB of hot-deformed magnet by Nd-Cu diffusion technique. The amount of infiltrated nonmagnetic Nd-Cu into hot-deformed magnet was controlled by expansion constraint diffusion technique. As a result, we could obtain high coercivity as same as 4% Dy containing sintered magnet with high remanence. Obtained magnet possesses higher maximum energy product than 4% Dy containing sintered magnet at 200˚C without Dy. The next step of this work is to realize a magnet with $H_c > 0.8$ T and $(BH)_{max} > 150$ kJ/m^3 at 200 ˚C.

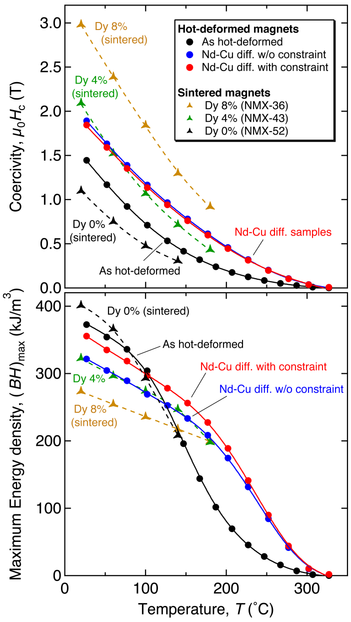

Fig. Temperature dependence of coercivity and maximum energy density.

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